

Organometallic Chemistry of Fullerenes: η^2 - and η^5 -(π)Complexes

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ABSTRACT: The reactivity of the fullerenes is primarily a function of their strain, as measured by the pyramidalization angle or curvature of the conjugated carbon atoms. A consideration of the orientation of the π -orbitals shows that η^2 -complexation reactions lead to reaction products with the fullerenes that are very similar to those obtained from unstrained alkenes. Furthermore, a large amount of strain energy is released in this reaction, so it is clear just why this reaction is important in fullerene chemistry. On the other hand, it is shown that the π -orbitals of C_{60} are poorly oriented for overlap with an exohedral metal atom centered over the five- or six-membered rings, but well disposed for overlap with an endohedral metal atom centered under the five- or six-membered rings. © 1998 John Wiley & Sons, Inc. *J Comput Chem* 19: 139–143, 1998

Introduction

It is well known that the chemistry of the fullerenes is characterized by addition reactions.^{1–4} The fullerenes undergo such reactions with relative ease because the conversion of trigonal carbon atoms to tetrahedral carbon atoms serves to release the tremendous strain present in the spheroidal geometry.⁵

It is straightforward to understand how σ -bond formation will be assisted by the geometry of the carbon atoms by a consideration of the POAV1 pyramidalization angle (θ_p). In POAV1 theory the π -orbital axis vector is defined to be that vector

that makes equal angles to the σ -bonds at a conjugated carbon atom. As can be seen in Figure 1, the C_{60} POAV pyramidalization angle of $\theta_p = 11.64^\circ$ is actually closer to the ideal tetrahedral angle than to the planar geometry required for the ideal trigonal angle.

Thus, it is clear that a chemical reaction that converts trigonal carbon atoms to tetrahedral carbon atoms will receive a very large steric assistance due to the relaxation of the strain in the cage. In fact, in an idealized analysis it was concluded that at least 20 carbon atoms would have to be converted to tetrahedral bonding in order to absorb the curvature and strain in C_{60} .⁵ Thus it is clear that the organic functionalization reactions that lead to σ -bond formation with the fullerene carbon atoms will receive a very large steric accel-

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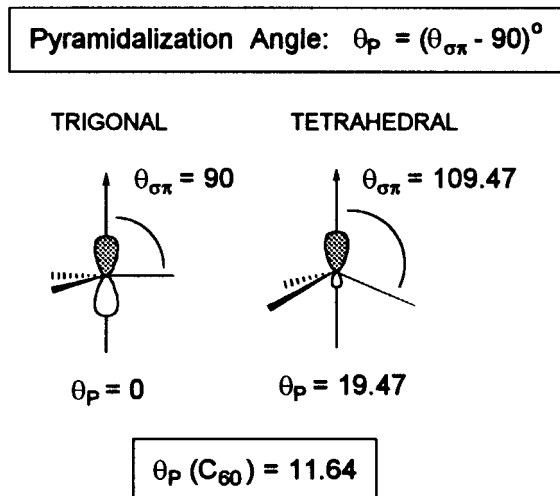


FIGURE 1. Schematic representation of pyramidalization angle.

eration in comparison with unstrained substrates. In this way the stability associated with the aromatic nature of the fullerene topology is masked by the countervailing drive of the fullerenes to relieve strain.⁵

In this article, we focus on the organometallic chemistry of the fullerenes. It has been known since the earliest work on fullerene chemistry that η^2 -complexes are readily formed and isolated.^{6–12}

Given the presence of five-membered rings (5-MRs) in the fullerenes, why is there not a well-developed class of pentahapto η^5 -complexes? We first begin with a review of the steric assistance received by the η^2 -complexation reaction.⁵ The strain energy analysis of the formation of $(\text{Ph}_3\text{P})_2\text{Pt}(C_{60})$, using the structure reported by Fagan and coworkers,⁶ is shown in Figure 2. For comparison purposes we make use of the structure of $(\text{Ph}_3\text{P})_2\text{Pt}(\text{Cl}_2\text{C}=\text{CCl}_2)$,¹³ as a representative example of η^2 -complexation of an unstrained alkene. The POAV1 strain energy analysis of this process is diagrammed in Figure 2.⁵

The strain energy analysis is divided into two parts: the local and global terms.⁵ The local term originates from the atoms that undergo changes in geometry as a result of direct coordination or bonding to the substituent—in this case the two atoms coordinated to the platinum atom. The global term reflects the changes in geometry of the remaining atoms in the fullerene—in this case the 58 atoms not coordinated to platinum. Although it might be expected that the only atoms undergoing a change in geometry would be those at the point of attachment this is not the case, because curvature, pyramidalization, and hybridization are approximately conserved in the fullerenes.^{5,14–16} Given the fact that the two atoms

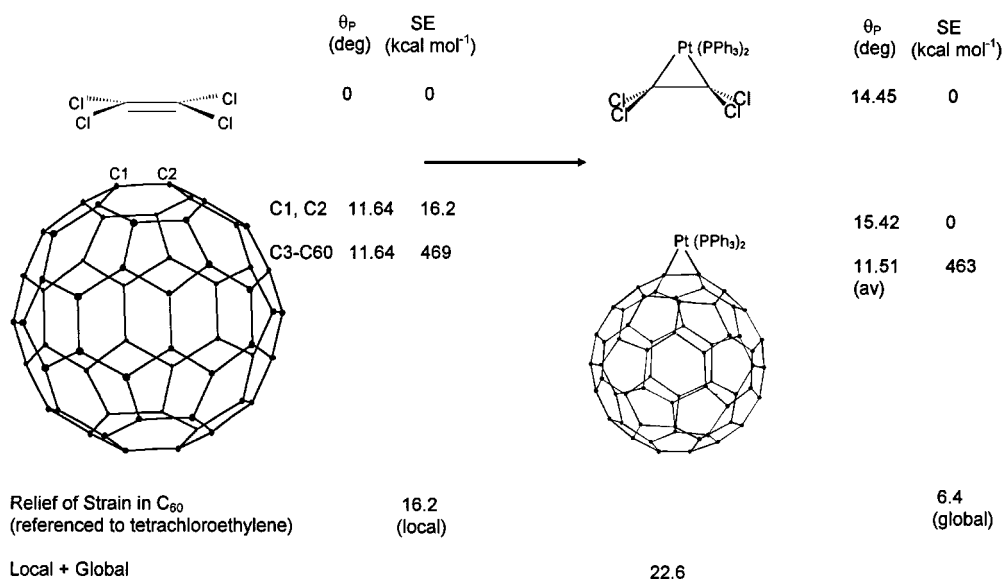


FIGURE 2. POAV1 strain energy analysis⁵ of the formation of $(\text{Ph}_3\text{P})_2\text{Pt}(C_{60})$.⁶ For comparison purposes, the same analysis is applied to the structure of $(\text{Ph}_3\text{P})_2\text{Pt}(\text{Cl}_2\text{C}=\text{CCl}_2)$,¹³ as a representative example of η^2 -complexation of an unstrained alkene. The strain energy (SE) is obtained from the relationship $\text{SE} = 196 \times \theta_P^2$ kcal/mol, where θ_P is expressed in radians.¹⁷ The local strain relief pertains to C1 and C2, the points of attachment of the metal. The global strain relief refers to strain relaxation that occurs in the other 58 carbon atoms due to the fact that complexation increases the pyramidalization at C1 and C2, and thereby reduces the strain at the remaining carbon atoms.⁵

at the point of attachment become more pyramidalized (θ_p increases from 11.64° to 15.42°), the amount of pyramidalization required at the other carbon atoms is reduced [θ_p decreases from 11.64° to 11.51° (average)]. Although the reduction in pyramidalization is small, because it is spread over 58 carbon atoms, it can have a large effect.⁵ Note that it is this term that is responsible for fullerene selectivity. Because the average carbon atom is less pyramidalized the substituted fullerene is less reactive. However, due to the loss of symmetry, some carbon atoms may become more pyramidalized and the selectivity issue requires an examination of the individual carbon atom pyramidalization angles.

Using the relationship $SE = 196 \times \theta_p^2$ kcal/mol (θ_p radians),¹⁷ the analysis presented in Figure 2 clearly shows that the formation of fullerene η^2 -complexes receives a considerable steric acceleration. In the present case this amounts to almost 23 kcal/mol, most of which will be available in the early stages of the reaction and serve to lower the transition state energy. We now turn to a consideration of the η^5 - and η^6 -complexation reactions and their geometric demands. In this case, the curvature of the fullerenes works against the coordination chemistry, basically because the orbitals are skewed outward from the centers of the 5- and 6-MRs, and the simultaneous overlap of the metal with all 5 or 6 of the ring π -hybrids is ineffective.^{5,6} In fact it is possible to solve for the orientation of the π -hybrids with respect to the normals to the planes of the 5- and 6-MRs (Table I). The direction of the π -orbital axis vector according to POAV1 theory is given above; the POAV2 π -orbital axis vector is obtained by construction of the hybrid orbital that is locally orthogonal to the σ -orbitals at a conjugated carbon atom.¹⁸ Due to the symmetry, in the case of the 5-MR, the POAV2 makes an angle of 106.3° to a vector from the center of the ring to the carbon atom, such that the POAV is directed radially away from the ring center. Thus the π -orbitals are poorly oriented for η^5 - and η^6 -complexation reactions, and improvement of the overlap would increase the strain. Recent experimental work supports this general picture.

A 6-MR face-capping arene-like complex of C_{60} has recently been isolated and characterized: $Ru_3(CO)_9(\mu_3-\eta^2, \eta^2, \eta^2-C_{60})$.¹⁹ In this complex all three of the partial double bonds in a single 6-MR are complexed in dihapto fashion. Thus, with the spread in π -orbitals it is possible to complex three metal atoms to the 6-MR.

TABLE I. Orientation of C_{60} π -Orbital Axis Vectors (POAVs).

Angle of POAV to:	POAV1 (deg.)	POAV2 (deg.)
5–6 Bond ^a	101.6	99.5
6–6 Bond ^b	101.6	105.5
Normal to 5-MR	20.1	16.3
Normal to 6-MR	23.8	25.8

^aBond that separates 5- and 6-MRs.

^bBond that separates two 6-MRs.

A pentahapto metal complex of a fullerene derivative was recently isolated and characterized: $Tl(\eta^5-C_{60}Ph_5) \cdot [2.5 THF]$.²⁰ We analyze the structure of this compound in some detail in what follows; further consideration of η^6 -complexation reactions is deferred to a later study, although it is of interest to note that the directionality of the π -orbital axis vectors favors coordination of the 5-MRs over the 6-MRs.

In Figure 3 we show the pyramidalization angles of the pentaphenyl-fullerene anion in this complex, as calculated from the structure supplied by the investigators.²⁰ The phenyl groups are omitted from the structure, but their point of substitution on the fullerene is indicated by solid circles. It is immediately apparent that these carbon atoms absorb a large fraction of the curvature or pyramidalization. In fact these carbon atoms are pyramidalized considerably beyond the tetrahedral pyramidalization angle of $\theta_p = 19.47^\circ$, and this is the most pyramidalized derivative to be examined. The pyramidalization angles in the bottom half of the molecule are changed little from those in the free C_{60} molecule. The net result is to flatten the upper carbon atoms in the fullerene—those toward the Tl^+ atom and particularly those atoms in the 5-MR that are actually complexed by the metal atom. This strongly suggests that the pyramidalization in free C_{60} is the determining factor in inhibiting η^5 -complexation.

This point is further reinforced by a consideration of the inclination angles made by the π -orbitals to the radial vector in the plane of the 5-MR as shown in Figure 4. Using POAV2 theory, the angle of 106.3° in free C_{60} , drops to 98.5° in the thallium complex. Thus, it is clear that the pentaphenyl substitution greatly improves the orbital overlap between 5-MR π -orbitals and the metal atom, to the point that the η^5 -complex is now stable.

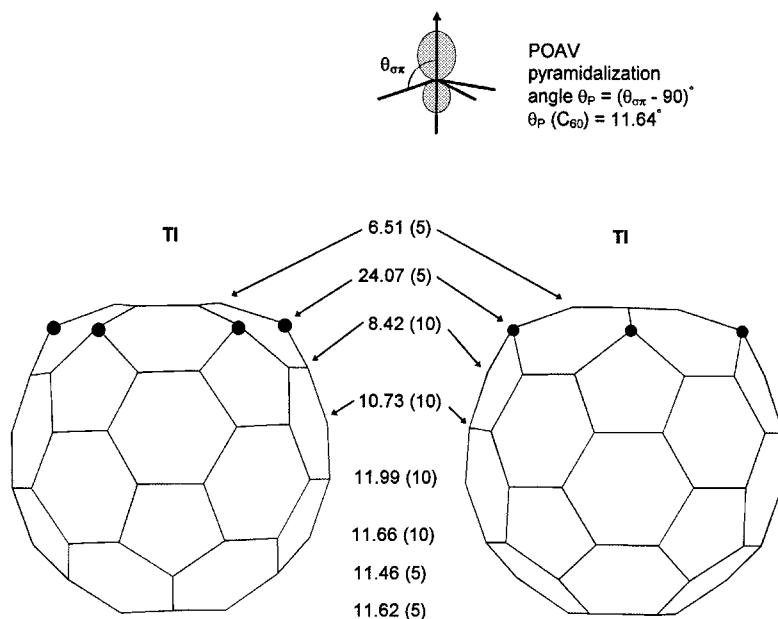


FIGURE 3. POAV1 pyramidalization angles of the $\text{Ti}(\eta^5\text{-C}_{60}\text{Ph}_5) \cdot [2.5 \text{ THF}]$ structure,²⁰ averaged over the pseudo-fivefold axis. The numbers in parentheses refer to the number of carbon atoms.

Hirsch and coworkers have shown that σ -bond formation with the concave face of the C_{60} molecule is strongly inhibited due to the strain that would be present in the product.²¹ The only apparent exception to this behavior is the suggestion that steric crowding on the convex surface of $\text{C}_{60}\text{H}_{60}$ leads to a preference for some fraction of the hydrogen atoms to bond to the concave surface.²² It is known that σ -bond formation and η^2 -complexation reactions readily occur on the convex face.^{1-4,23} This is shown schematically in Figure 5, along with the present results which suggest that η^5 - and η^6 -complexation reactions prefer the opposite face—that is, the concave face due to considerations of orbital overlap.

An alternative viewpoint of this process is shown using the sense of the π -orbital axis vector. The positive sense of the POAV is defined to lie toward that lobe of the p -orbital that has the same sign as the s -orbital.²⁴ Thus, reactants that have a low nuclearity on the fullerene and form strong bonds to one or two atoms will be favored by a positive sense of the POAV due to the divergence of the orbital hybrids. On the other hand, reactants with a high nuclearity (involving five or six atoms) will be favored by a negative sense of the POAV, which leads to convergence of the orbitals in the interior of the fullerene.

This behavior may not hold at small pyramidalization angles, such as those found in the outer 6-MRs of corannulene, as a recent study provides computational evidence for complexation of an $\text{Ru}(\text{Cp}^*)^+$ fragment on the concave face of the coran-

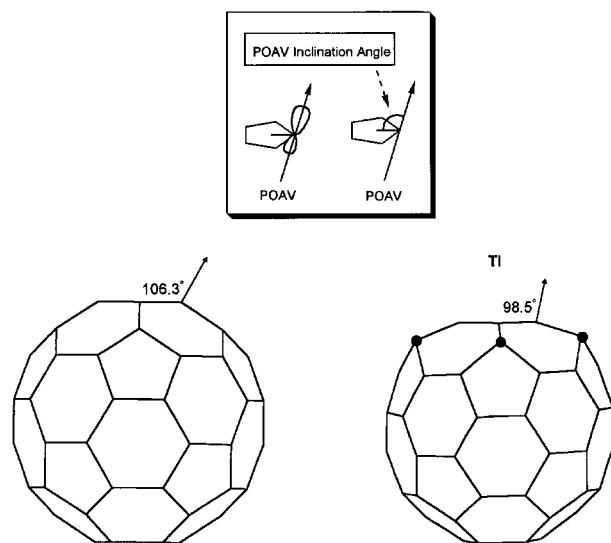


FIGURE 4. Inclination of the POAV2 to the radial vector of the 5-MR in C_{60} and in the $\text{Ti}(\eta^5\text{-C}_{60}\text{Ph}_5) \cdot [2.5 \text{ THF}]$ structure.²⁰ With POAV1 theory the values are: 111.1° (C_{60}), 101.1° (complex).

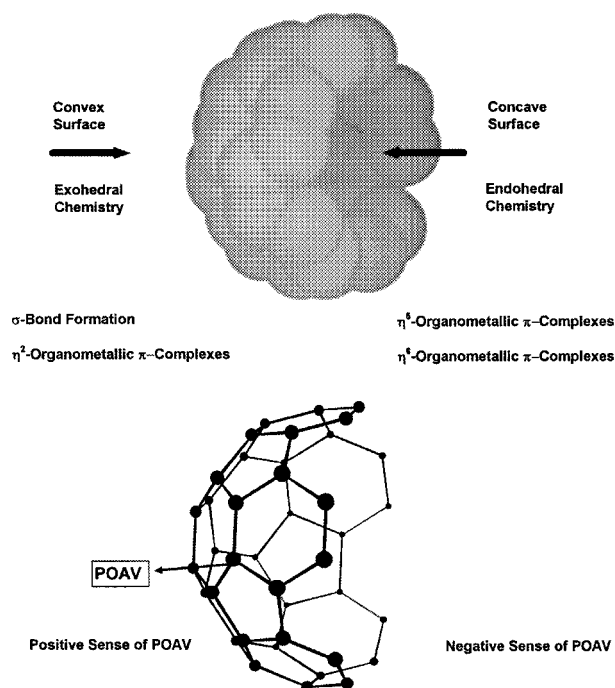


FIGURE 5. Fullerene reactivity with respect to chemistry on the outside and inside of the fullerenes.

nulene molecule (although the analysis is complicated by steric congestion).²⁵

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